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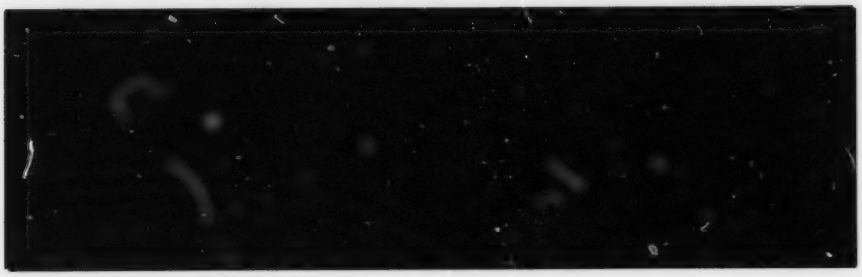

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THE EXPLOSION ON THE SHIP "POLLUX" AT PORT ALFRED, QUEBEC MARCH 19, 1990: A LABORATORY INVESTIGATION

K.J. Mintz

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MICROMEDIA

THE EXPLOSION ON THE SHIP "POLLUX" AT PORT ALFRED, QUEBEC, MARCH 19, 1990: A LABORATORY INVESTIGATION

by

K.J. Mintz*

ABSTRACT

"Spent potlining", also called potlining mix, etc., a waste product from Alcan, became wet prior to and during loading of the ship, generating explosive gases. The explosive gas mixture in the cargo hold was probably ignited by an electric spark from the switchbox controlling the hatch cover. Laboratory tests confirmed that spent potlining do produce explosible quantities of hydrogen and methane by reaction with water. Details of the tests are provided in this report. However, the United Nations tests for "substances which, in contact with water, emit flammable gases" (Dangerous Goods, Division 4.3) indicate that spent potlining should not be so classified. An analysis of the U.N. tests for this category shows that they are inadequate; it is recommended that these tests be revised, both in procedure and in the limits specified.

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*Research Scientist, Canadian Explosive Atmospheres Laboratory, Mining Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa

EXPLOSION DU "POLLUX" À PORT ALFRED (QUÉBEC), LE 19 MARS 1990: INVESTIGATION EN LABORATOIRE

par

K.J. Mintz*

RÉSUMÉ

Le revêtement de cuve usé ("les brasques"), un résidu d'Alcan, s'est humidifié avant et pendant le chargement du navire, produisant ainsi des gaz explosifs. Le mélange de gaz explosifs dans la soute à fret s'est probablement enflammé sous l'effet d'une étincelle électrique dans la boîte d'interrupteurs commandant le panneau d'écoutille. Les essais en laboratoire ont confirmé que le revêtement de cuve usé réagit effectivement avec l'eau pour produire des quantités d'hydrogène et de méthane suffisantes pour provoquer une explosion. Les essais sont décrits en détail dans le présent rapport. Selon les normes des Nations Unies pour les "substances qui, au contact de l'eau, dégagent des gaz inflammable" (Matières dangereuses, Division 4.3), le revêtement de cuve usé ne doit pas être classifié. Cependant, une analyse des essais de l'ONU concernant cette catégorie montre que les essais sont inadéquats. Nous recommandons que ces essais soient corrigés, à la fois du point de vue de la méthode et des limites prescrites.

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*Chercheur, Laboratoire canadien de recherche sur les atmosphères explosives, Laboratoires de recherche minière, CANMET, Énergie, Mines et Ressources Canada, Ottawa.

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THE MATERIAL "SPENT POT LININGS"

Aluminum is produced by the electrolysis of its oxide (alumina). The cathode of the cell is made from carbon, which also acts as the cell lining. Molten aluminum is deposited on these cathodes and removed from the cell. The carbon cathode is consumed during the electrolysis (1). At some stage, these carbon cathodes are no longer effective and must be removed; they become the waste product in question. Aluminum and other substances are absorbed into or adsorbed onto these carbon cathodes and thus are part of the "potlining mix" (referred to in French as "brasques"). Because of the nature of the process, some cathodes last much longer than others. Upon removal, these potlinings have proportionately much less carbon. Hence, the composition of this waste product is very variable.

The Material Safety Data Sheet (MSDS) for this material is in Appendix A. The concentration ranges of the ingredients are listed on p. A1. It should be emphasized that "total sodium" does not refer to free sodium metal but rather to sodium ions as part of compounds. Sodium metal is very reactive, whereas sodium ions are quite inert. From the chemical reactivity viewpoint, the ingredients to note are aluminum and carbon. The "aluminum" referred to in the table refers to total aluminum, free (metallic) plus chemically bound (in the form of aluminum oxide). Aluminum oxide is quite inert; it is only the metallic aluminum that is of interest here. It comprises in the order of 1% of the pot linings on a mass basis.

BRIEF DESCRIPTION OF THE EVENTS

Workers loading the cargo of spent potlining onto the ship reported having smelled ammonia and crew members were reported to have been bothered by its smell. Some of the loading was reported to have been carried out in rain or snow. The vent trunks and fan

room access to the ship's hold were covered with plastic. Hold #1 of the ship exploded at about 2:30 p.m. on March 19, 1990, blowing off the hatch cover, thereby killing two people, seriously injuring a third, and causing several minor injuries ashore. Extensive damage was caused to the ship as well as some damage to the roofs and windows of a warehouse shed and office building adjacent to the docks. The explosion was heard several kilometres away, with some glass breakage in the town.

In the case of most explosion investigations, the explosive gases have disappeared by the time that the investigators have reached the site and they have to be determined by indirect means. In this situation, however, hold #2, which did not explode, still contained explosive gases. Analyses by Alcan (by gas chromatography) showed significant concentrations of hydrogen, methane and ammonia, and traces of acetylene. For example, one analysis yielded 0.9% hydrogen, 0.5% methane and 0.2% ammonia. There was concern that the presence of explosive gases in hold #2 (which still had the hatch cover in place) could cause another explosion. In order to prevent any spark from igniting the gas mixture, no attempt was made initially to raise the hatch cover of hold #2. Instead, an attempt was made to inert hold #2 by flooding with carbon dioxide. This did not work; in fact, the technician taking samples from hold #2 for analysis reported that warm air was coming out of the hold. When the CO_2 addition was stopped, the concentrations of hydrogen and methane started decreasing. It seems possible that the CO_2 was taking part in a process which generated heat; the higher temperature would have increased the rate of production of methane and hydrogen.

A confusing factor which caused some delay and concern was the disagreement between the gas analysis (carried out on grab samples by gas chromatography by the Alcan laboratories) and the portable flammability meter inserted into the hold. The lower explosible limits (LEL) of pure hydrogen, methane and ammonia are, respectively, 4.0, 5.0 and 15.0, expressed as percentage by volume

in air (2). To calculate the LEL of a mixture of explosive gases from the gas chromatographic analysis, Le Chatelier's Law (2) is used:

$$LEL = \frac{100}{\left(\frac{C_1}{LEL_1} + \frac{C_2}{LEL_2} + \cdots\right)}$$

where LEL_1 is the LEL of component 1, C_1 is the percentage of component 1 in the explosive gas portion, etc. For example, for the analysis of gases from hold #2 given above, hydrogen was 56%, methane 31% and ammonia was 13%, of the explosive gas portion. Then, Le Chatelier's Law yields 4.7% as the LEL of that mixture. The total of the three gases was only 1.6%, which therefore was 34% of the LEL. The flammability meter reads the percentage of the LEL directly; it always indicated much higher values, usually about double that calculated from Alcan's gas chromatographic analysis. Eventually, the gas chromatographic results were accepted as being correct and the hatch cover of hold #2 was raised (in the early morning of March 23) without incident.

HISTORY OF THE MATERIAL

Spent potlining was reported to have been stored both outside and inside a building. The smell of ammonia from the latter was reported to be apparent, until forced air ventilation was installed. Alcan reported that, up to some years ago, they recycled the material. Alcan reported that minor explosions had occurred in their ball mill during grinding of spent potlining, until ventilation was installed.

Spent potlinings are a problem with all aluminum producers. Alcoa is reported to have carried out laboratory tests to measure the quantity of explosive gases generated by this material. Unfortunately, their results are not accessible, because their

report is not in the public domain, having been circulated only within the industry. Ground-up potlinings is said to generate 1 - 2 mL/g/hour. The theoretical amount of hydrogen that could be produced, assuming all of the aluminum reacts, is about 12 mL/g total.

Augood of Kaiser Aluminum (3) has published the results of a study on reaction of spent potlining with water. With some samples, more methane was generated than hydrogen, in others, vice versa. In all cases, ammonia was produced in the largest amount, and negligibly small amounts of other saturated and unsaturated hydrocarbons were also produced. The total amount of gas generated was about 188 mL/g. At ambient temperature, the rate of reaction was 2.7, 1.3 and 0.8 mL/g·h for particle sizes of 0.15, 2.6 and 19 mm, respectively.

LABORATORY STUDIES

In order to confirm that spent potlining is capable of generating explosive gases, three samples were taken by officials of Transport Canada: from Hold #1, from the pile stored outside, and from inside the storage building. The samples were sent to laboratories in Quebec and Ontario. Each laboratory crushed the samples and tested for evolution of flammable gases. In neither case was any flammable gas produced by contact with water; the Ontario laboratory found that a small amount of ammonia (well below the LEL) was produced when the sample was immersed in a strong alkali solution. The Quebec laboratory tested to determine if spent potlining would be classified under the United Nations Code for substances that emit flammable gases when exposed to water (Division 4.3). The answer was a definite negative.

In order to resolve the contradiction between the two laboratory results, on the one hand, and the fact that an explosion did occur, on the other hand, the samples from the Quebec laboratory (both the crushed and the original material) were sent

to this laboratory for further study.

The sample from hold #1 had a few orange pieces in it. These are from the clay lining and are non-reactive. Some of the pieces were black and crumbly all the way through, others were black on the outside with hard, white material inside. A few pieces had some metallic portion inside. The sample from the outside pile had greyish lumps, with either white material or metallic material inside. The sample from the inside pile was similar to the outside pile. All samples, which were received in jars with fairly tight-fitting lids, had a definite ammonia smell; sample from hold #1 had the strongest odour.

The four tests described in the U.N. regulations (Appendix B) for Division 4.3 - "substances which, on contact with water, emit flammable gases" were carried out on the three samples (crushed). No indication of a positive result was obtained.

A few grams of each sample (crushed and original) was placed into a beaker containing distilled water. After an hour, tiny bubbles could be observed on the surfaces of particles of all the samples except the crushed sample from the outside pile. By 20 hours, that one had the bubbles as well. These bubbles generally remained fixed for a long time to the particles. This was the first laboratory evidence that gases were being generated by potlining.

To measure the type and quantity of gases generated, samples of the materials were placed in distilled water in an Erlenmeyer flask which was connected to an inverted burette filled with water and immersed in a trough of water. Any gases generated would displace the water in the burette; the volume could then be read directly.

Using 25 g of each of the three crushed samples, no gas evolution could be measured at room temperature over 24 h.

The water content for each of the three crushed samples was estimated by measuring the weight loss at 140°C. The values obtained were: 14% for the sample from hold #1, 7% for the sample from the outside pile and 13% from the inside pile. These values are in good agreement with the values obtained by the Quebec laboratory.

It was thought that the moisture might be deactivating the surfaces of the particles. Therefore, the gas evolution tests were repeated using the crushed samples that were dried prior to testing. The sample sizes used were increased to approximately 100 g, in order to increase the quantity of gas evolved.

The results were quite variable, no doubt due to the variability of the material. On the sample from the inside pile, three tests yielded 0.01, 0.02 and 0.035 mL/g.

In order to speed up the tests, as well as to be able to collect enough sample for gas analysis, a number of tests were carried out with the sample heated up to about 60°C for about two hours. The results of the tests, together with room temperature tests run for about 20 hours, are shown in the following table:

Table 1. Volume of gas (in mL) produced per gram of "spent potlining"

	Crushed sample				Sample as received			
	dried		not dried		dried		not dried	
	22°C	60°C	22°C	60°C	22°C	60°C	22°C	60°C
hold #1	0.08	0.25	0	0.05	0.02	0.7	--	0.1
outside pile	0	0.3	0.01	0.3	--	--	0 14	0.55
inside pile	0.01 - 0.035	0.1*	0	0	--	--	0.01	0.14

*tested at about 40°C

The data show that, generally, pre-drying the sample increases the quantity of gas generated, and that temperature increases the rate of gas evolution. At the lower temperature prevailing at the time of the incident, the rate of reaction would have been somewhat less than that measured in the laboratory at room temperature. The most important fact remains that all three samples generate gas. Because of the intrinsic variability of this material, it would be risky to interpret the numbers any further.

A 60 g sample of the inside pile was dried by heating, then placed in a 250 mL Erlenmeyer flask with 80 g distilled water. The free air volume was about 140 mL. After an hour, the gas above the mixture was passed through an infrared methane analyzer; the reading was 3.1% methane. If the free air volume had been smaller, the concentration of methane would have easily exceeded the LEL of 5%.

Another sample of the inside pile was treated in a similar manner except that the mixture was heated to generate more gas, so that it could be analyzed by gas-liquid chromatography. The result was: 19% hydrogen and 14% methane, which is well above the LEL. The ratio of hydrogen:methane is consistent with analyses of the gas in hold #2, which were in the range of 1.5 - 2.

Finally, 170 g of the sample from the inside pile was placed in a 250 mL Erlenmeyer flask with 180 g distilled water and closed with a rubber stopper. The free space above the mixture was roughly 10 mL. After two days at room temperature, the stopper was removed and a lit match was placed in the mouth of the flask. The mixture was stirred, causing a number of large bubbles to rise to the surface. A series of "pops" were heard, proving the existence of flammable gases. After leaving it closed for another four days, a lit match, when inserted into the air above the mixture, produced a louder "pop" plus a small, brief flame. The other samples were tested in the same way. They also produced "pops", sometimes with accompanying flames, after being left stoppered for four days at

room temperature.

DISCUSSION OF LABORATORY RESULTS

The above laboratory results show conclusively that explosive gases, hydrogen and methane, can be produced by the reaction of spent potlining with water, whether the material was from hold #1 of the "Pollux", outside storage or inside storage. Prediction of the actual quantity of gas generated is difficult because of the intrinsic variability of the material, the size and surface conditions of the particles (which would be modified by the transportation and loading equipment used), and the quantity of water present. The important point, however, is whether the hypothesis that sufficient explosible gases could be generated to create an explosive mixture is reasonable.

According to information supplied by Mr. Eric Snow, of the Canadian Transportation Accident Investigation and Safety Board, the volume of hold #1 was 4715 m^3, with attached fan rooms of volume 1158 m^3. The mass of cargo was 2150 Tonnes, which corresponds to a volume of 1000 m^3, assuming a density of about 2.2. Thus the free space would have been about 4870 m^3. Assuming that the quantity of gas generated was 0.1 mL/g*, then the total volume of gas produced would have been 215 m^3. The resultant concentration would be about 4.4%, close to the LEL of the gas mixture which would be 4.4%. This illustrative calculation demonstrates that the above hypothesis is reasonable, based on the laboratory measurements.

The reader may have noted that the rate of gas generated was much less than the 1 - 2 mL/g/h reported to have been obtained in laboratory tests by Alcoa, and the 0.8 - 2.7 mL/g/h reported by

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*It should be noted that the hatch cover had been in place about 4 days prior to the explosion, thus allowing sufficient time for the explosible gases to be generated.

Augood. The difference is probably due to the less ideal conditions employed in the present study, e.g. the material was not stirred during the test, thus diminishing the contact between fresh surfaces and the water. However, this better simulates the process that occurred in the ship.

MECHANISM OF THE EXPLOSION

Aluminum powder is well known to generate hydrogen, a highly explosive gas, if it is placed in contact with water (4). The other explosive gases generated, methane and ammonia, are difficult to explain from the composition of spent potlining that is given in the MSDS. However, aluminum carbide is known to produce methane on contact with water (5). Similarly, aluminum nitride is known to produce ammonia on contact with water (5). It is quite likely that both aluminum carbide and nitride are present in spent potlining. Although the qualitative aspects of the gases produced would be expected to remain the same for all samples of potlining, the quantitative aspects would be expected to differ significantly because the pots may have been operated for different times and spent potlining may have been stored under different conditions.

The ignition source for the explosion was probably a spark from the switch for the motor operating the opening of the hold cover. Photographs of the switch boxes, provided by Mr. L. Vacher of the Canadian Transportation Accident Investigation and Safety Board, show that one box was heavily damaged, whereas the other was not. The damage to the inside of the first switch box is consistent with an explosion of combustible gases inside the box. The resulting flame front could then have travelled into the hold igniting the gas therein with the resultant observed damages. Only if the switch and motors were explosion-proof rated to Class I, Group B (U.S./Canada) or Group IIC (International) could the first possibility be ruled out. Note that explosion-proof ratings of Class I, Groups C or D would not necessarily be adequate in this case, because the main species of concern is hydrogen, which has a

lower ignition energy and a higher rate of reaction than most other explosive gases.

Another question that can be raised is: would there have been sufficient energy in the gas mixture generated to propel the massive steel hatch cover high into the air? Of course, since the concentration of gases at the time of explosion is unknown, it is impossible to calculate the exact answer. But a calculation of the energy involved, assuming that the concentration of explosible gases is near the lower explosible limit, is useful to determine whether the mechanism is reasonable. From the numbers in the previous section, there would have been about 12 kg of hydrogen and 61 kg of methane. The heat of combustion is 29 kcal/g for hydrogen and 13 kcal/g for methane. Thus, the total energy available is about 5×10^9 J. The energy, E, required to raise an object against the force of gravity is given by:

$$E = mgh$$

where m is the mass of the object, g is the acceleration due to gravity and h is the height. According to information supplied by Eric Snow, the total mass of the hatch covers of hold #1 was 110 Tonnes. If all the energy went into projecting the hatch cover upwards, then the equation predicts that the cover would rise to 4000 m. However, considerable energy was used to snap off the seatings as well as project the pistons (used for operating the hatch covers), which would lower the maximum height possible. Furthermore, not all the energy would have been directed upwards. The evidence is that the forward sections of the hatch covers cleared the foremast (20 m) and the aft sections of the covers hit and damaged the crane. Although the calculation is indicative rather than quantitative, it does demonstrate that there was sufficient energy in the explosion of the hydrogen/methane mixture to propel the hatch covers well up into the air.

TRANSPORTATION OF DANGEROUS GOODS

The question is: does this material fall into the "dangerous goods" category? Division 4.3 is for "substances which, in contact with water, emit flammable gases". Note that a substance is so classified only if at least 1 L of flammable gas per kg per hour is generated (see Appendix B).

The Workplace Hazardous Material Information System (WHMIS) classification, according to the MSDS from Alcan, is D2B. The D2 refers to being in Division 2 of Class D, "toxic materials", which is not of interest here. "B" refers to Class B -"flammable and combustible material". Presumably, it falls into Division 6 of Class B "reactive flammable materials". This is defined as follows: "it emits a flammable gas or becomes spontaneously combustible on contact with water or water vapour" (6). Note that no test is specified, therefore **any** quantity of flammable gas would be sufficient to so classify a material. This is in marked contrast to the Transport of Dangerous Goods Classification, which requires a significant quantity of gas to be generated.

Augood's study (3) as well as the Alcoa work referred to above suggests that spent potlining **might** fall under the dangerous goods classification, though the present laboratory investigation indicates that it does not. However, the fact remains that the gases produced by the cargo did explode. The problem in making a decision based upon the existing dangerous goods classification would be the extreme variability of the material. Apart from the variability from the source, the moisture content and the amount of weathering greatly affect the rate of generation of explosible gases.

The U.N. test, referred to above, is sufficiently simple that almost any chemical laboratory could carry it out. However, it appears to suffer from serious deficiencies. Firstly, it does not differentiate between different explosive gases. For example,

as mentioned above, hydrogen has an LEL of 4%, whereas ammonia has an LEL of 15%. Secondly, the specified limit of 1 L/kg/h is, in the writer's opinion, insufficient to guarantee a reasonable degree of safety, as shown by the following illustrative calculation.

Consider a 1 m^3 container. Assume a material with specific gravity of 2 (similar to the potlining), which generates methane, a typical explosive gas. Put 50 kg of the material into the container, which would fill up about 2.5% of its volume. Assume that the material generates just under 1 L/kg/h (the limiting value to be not classified). If the container is tightly closed, one hour later the concentration of methane inside the container will reach its LEL, and there is a possibility of an explosion. After two hours, the concentration of methane will be optimum to produce the strongest explosion.

As part of his study, Augood(3) calculated the possibility of the creation of an explosive atmosphere in a hopper car. His conclusion was that "given reasonable assumptions, it appears that said atmosphere is non-explosive". (He does go on to say that "it is important to keep potlining dry and/or ventilate any storage or transportation vessel".) It is instructive to examine Augood's calculations. He assumed a car of volume 112 m^3 containing 40 Tonnes of potlining with a density of 1730 kg/m^3. (This means that the potlining occupied only 23 m^3, or 20% of the total volume.) Augood also assumed that 40 kg of water leaked into the car, which would produce a gas mixture of less than half the LEL. However, if the free space were cut in half (i.e. the potlining occupied 40% of the car), then the gas mixture would approach the LEL, and Augood's conclusion would no longer be valid.

It is the writer's understanding that classifying goods as "dangerous" is not to prevent their transportation, but rather to ensure that they are transported in a safe manner. Thus it is important that any laboratory test be capable of determining if a material is potentially dangerous and under what conditions. It is

clear, based upon the fact of the explosion on the "Pollux", as well as from the discussion above, that the U.N. test for Div. 4.3 is inadequate and should be revised, with respect both to procedure and to the specified limits. The limit should take into account the maximum size of cargo holds and the possible energy from an explosion of the flammable gas generated, in other words, would the explosion be sufficiently strong to damage the structure of the cargo hold.

Continuous adequate ventilation will, of course, prevent any problem with build-up of explosive gases. In this context, it is necessary to examine how safe it is to handle this material in the laboratory. Consider a small laboratory 5 m by 5 m by 3 m high. If 10 kg of this material were brought into this laboratory and immersed in water, the rate of gas generated would be less than 10 L/h. Even if the ventilation were very poor, say, one exchange of air per hour, the concentration of flammable gas would only reach in the order of 0.01%, which is far below the LEL. Danger would arise only if the material were stored wet in a closed container for a substantial period of time and, when the container was opened, there was a suitable source of ignition in the vicinity. It is therefore much less hazardous than common solvents used in a chemical laboratory. Nevertheless, the containers should be labelled because of the possibility of explosible gases generated, as well as the toxic hazard from ammonia which, as noted earlier, is also generated, plus the toxic hazard from the solid material itself. For transportation, the important points are that the material should be shipped dry and should be packaged so that they will not come into contact with water under normal and specified abnormal conditions.

The question has been raised as to whether spent potlining should be considered as "aluminum dross". One reference defines dross as a metallurgical term: "an impurity formed on the surface of a molten metal" (7). Another reference gives both a metallurgical definition "a waste product taken off molten metal

during smelting, essentially metallic in nature", and a general definition "waste matter; refuse" (8). Although one could argue that spent potlining falls into the latter category, it seems more reasonable to say that spent potlining should **not** be referred to as aluminum dross, not just because of the definitions, but because the hazard of spent potlining arises from the carbon and other components of this material, as well as from the aluminum. Hence, spent potlining should have its own category.

ACKNOWLEDGEMENTS

Penny MacDonald of the Energy Research Laboratories, CANMET, carried out the gas chromatography analysis.

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MATERIAL SAFETY DATA SHEET

IDENTIFICATION

PRODUCT NAME : SPENT POTLINING

AHMS NUMBER : A0026 REVISION DATE : 07/03/9

SUPPLIER :
ALCAN SMELTERS AND CHEMICALS LTD
SUBSIDIARY OF :
ALCAN ALUMINIUM LTD
1188, SHERBROOKE WEST BUSINESS PHONE: (514) 848-8000
MONTREAL (QUEBEC), CANADA EMERGENCY PHONE: (514) 848-1454
H3A 3G2

SYNONYMS :
SPENT CATHODES; POTLINING; BRASQUE USEE
REBUS DES CATHODES (SALLES DE CUVES);
SPENT POTLINING; WASTE OF CATHODS (POTROOMS)

APPEARANCE & ODOR :
SOLID GREY-BLACK WITH AMMONIA ODOR IF WET

USES :
WASTE PRODUCTS

INGREDIENTS

NAME	CONC.	CAS
CARBON	26-72%	7440-44-0
TOTAL SODIUM	13-17%	
FLUORIDES	7-22%	
CYANIDES	<0.7%	151-50-8
ALUMINUM (AL)	5-20%	7429-90-5
ALUMINA (AL2O3)	11-22%	1344-28-1
CALCIUM OXIDE (CAO)	< 3%	1305-78-8
SILICATES	<10%	
IRON OXIDE (FE2O3)	<1.4%	1309-37-1
MAGNESIUM OXIDE (MGO)	<.35%	1309-48-
TOTAL SULFUR	<0.2%	

DOES NOT CONTAIN ANY CARCINOGENS OR POTENTIAL CARCINOGENS -IARC,NTP,OSHA

WHMIS CLASSIFICATION: D2B

PHYSICAL DATA

EVAPORATION RATE	: N/A	(N/A	=1)		
BOILING POINT	: N/A	'C		VAP. DENSITY :	N/A (AIR =1)
MELTING POINT	: N/D	'C		SPEC. GRAVITY:	2.0-2.5(WATER =1
VAPOUR PRESSURE	: N/A	mmHg	'C	PARTIC. SIZE :	N/D
% VOLATILE (VOL)	: N/A			WATER SOLUBI.:	N/D g/l
				PH :	N/A

FIRE & EXPLOSION HAZARD

FLASH POINT	: (N/A)	N/A	'C	NFPA CODE : 1
AUTO-IGNITION TEMP	:	N/A	'C	
FLAMMABLE LIMITS	: LOW.:	N/A	%	
	UPP.:	N/A	%	

EXTING.MEDIA AND SPECIAL TECHN.:

COMBUSTIBLE.
DRY CHEMICAL AGENTS (CO2). DO NOT USE WATER.
SPREAD THE PRODUCT OUTSIDE AND COVER WITH SAND.
WEAR A SELF-CONTAINED BREATHING APPARATUS AS NECESSARY.
DO NOT USE WATER, THE REACTION WILL EMIT AMMONIA AND EXPLOSIVE GASES.

REACTIVITY

STABLE: X UNSTABLE:

CONDITIONS & MATERIAL TO AVOID:
AVOID CONTACT WITH WATER, ACIDS, BASES AND INTENSE HEAT.

HAZARDOUS POLYMERIZATION:
N/A

HAZARDOUS DECOMPOSITION:
AMMONIA AND EXPLOSIVE GASES (HYDROGEN, METHANE AND ACETYLENE) CAN BE RELEASED IF THE PRODUCT COMES IN CONTACT WITH WATER OR ALKALIS. FLUORIDES, HYDROGEN FLUORIDE, HYDROGEN CYANIDE AND OXIDES OF SULFUR CAN BE RELEASED IF THE PRODUCT COMES IN CONTACT WITH HIGH TEMPERATURES OR ACIDS.

HEALTH EFFECTS

ROUTES OF ENTRY	: INHALATION	: X		INGESTION	:X
	EYE CONTACT	: X		SKIN	:X
TARGET ORGAN(S)	: RESPIRATORY TRACT			BONES	
	DIGESTIVE SYSTEM			EYES	

SKIN

ACUTE TOXICITY:

INHALATION:

SEVERE IRRITATION OF THE RESPIRATORY TRACT.
IF HIGH CONCENTRATIONS OF AMMONIA ARE RELEASED, THEY CAN CAUSE BRONCHO-SPASM, DYSPNEA AND CHEST PAIN.

SKIN CONTACT:

IRRITATION.
FREE CYANIDES MAY BE ABSORBED THROUGH WET SKIN.

EYE CONTACT:

IRRITATION AND BURN.

INGESTION:

IRRITATION OF THE GASTRO-INTESTINAL TRACT, NAUSEA, VOMITING; IF THE AMOUNT INGESTED IS HIGH, DEATH CAN OCCUR.

CHRONIC TOXICITY:

PROLONGED OVEREXPOSURE TO FLUORIDES MAY INCREASE RADIOGRAPHIC DENSITY OF BONES AND TEETH AND WHICH CAN RESULT IN FLUOROSIS.

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MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE TO THE PRODUCT:
RESPIRATORY DISEASES.

SUPPLEMENTARY INFORMATION :

FOR PERSONS HABITUALLY EXPOSED TO THE DUST, AN ANNUAL PHYSICAL EXAM SHOULD BE GIVEN INCLUDING MEASUREMENT OF URINARY FLUORIDE.

THE AMOUNT OF URINARY FLUORIDE SHOULD NOT EXCEED 4 PPM (PRE-SHIFT) OR 7 PPM (POST-SHIFT).

EXPOSURE LIMITS :

	ACGIH (TLV)		OSHA (PEL)	
	TWA	STEL	TWA	STEL
FLUORIDE (AS F)	2.5 MG/M3	ND	2.5 MG/M3	ND
ALUMINUM (TOT.DUST)	10 MG/M3	ND	15 MG/M3	ND
-FUME,POWDER,RESP.DUST	5 MG/M3	ND	5 MG/M3	ND
ALUMINUM OXIDE (TOT.DUST)	10 MG/M3	ND	10 MG/M3	ND
-RESP. DUST	ND	ND	5 MG/M3	ND
IRON OXIDE FUME	5 MG/M3	ND	10 MG/M3	ND
MAGNESIUM(OXIDE+FUME TOT)	10 MG/M3	ND	15 MG/M3	ND
-RESP. DUST	ND	ND	5 MG/M3	ND
CYANIDE (AS CN)	5 MG/M3	ND	5 MG/M3	ND
HYDROGEN CYANIDE	10 PPM	10 PPM-CEIL	ND	4.7 PPM
CALCIUM OXIDE	2 MG/M3	ND	5 MG/M3	ND
SILICATES,AMORPHOUS	10 MG/M3	ND	6 MG/M3	ND
AMMONIA (NH3)	25 PPM	35 PPM	ND	35 PPM

FIRST AID MEASURES

INHALATION:
IN CASE OF DISCOMFORT BY VAPORS OR DUSTS, MOVE TO A VENTILATED AREA.
CONSULT A PHYSICIAN.
SKIN CONTACT:
REMOVE CONTAMINATED CLOTHES. WASH SKIN THOROUGHLY WITH SOAP AND WATER.

EYE CONTACT:
FLUSH EYES WITH ABUNDANT QUANTITIES OF WATER AND WASH CAREFULLY UNDER EYELIDS. CALL A PHYSICIAN.
INGESTION:
GIVE PLENTY OF WATER. INDUCE VOMITING IF THE PERSON IS CONCIOUS.

PREVENTIVE MEASURES

PERSONAL PROTECTION:
USE LOCAL AND GENERAL EXHAUST VENTILATION TO KEEP CONCENTRATIONS AS LO.. AS POSSIBLE.
USE A DUST MASK AND/OR A RESPIRATOR WITH AMMONIA AND PARTICULATE FILTERS IF AIRBORNE CONCENTRATIONS EXCEED THE THRESHOLD LIMIT VALUES.
WEAR PROPER PROTECTIVE CLOTHING TO AVOID CONTACT WITH WET SKIN.

USE NEOPRENE GLOVES TO AVOID SKIN CONTACT.

CHANGE WORK CLOTHING IF CONTAMINATED.

HANDLING METHODS:
KEEP THE MATERIAL DRY.
AVOID ALL SKIN AND EYE CONTACT.

STORAGE REQUIREMENTS:
STORE AWAY FROM ACIDS, BASES AND OXIDIZING MATERIALS.
STORE IN A COOL, DRY AND WELL-VENTILATED AREA.

SPILL, LEAK, DISPOSAL PROC.:
KEEP THE MATERIAL DRY.
SHOULD THE MATERIAL BECOME MOIST, ENSURE THE PH IS ALKALINE.
SMALL SPILL:
PUT INTO APPROPRIATE CONTAINERS.
AVOID POLLUTION OF SURFACE WATER, STREAMS OR SEWERS.

WASTE PRODUCTS SHOULD BE TESTED TO DETERMINE ANY HAZARDOUS CHARACTERISTICS.
DISPOSE OF THE WASTE IN ACCORDANCE WITH FEDERAL, STATE OR LOCAL WASTE DISPOSAL REGULATIONS.

ADDITIONAL INFORMATION:

THE INFORMATION IN THIS MSDS WAS OBTAINED FROM SOURCES WHICH WE BELIEVE ARE RELIABLE BUT CANNOT GUARANTEE. ADDITIONALLY, YOUR USE OF THIS INFORMATION IS BEYOND OUR CONTROL AND MAY BE BEYOND OUR KNOWLEDGE. THEREFORE, THE INFORMATION IS PROVIDED WITHOUT ANY REPRESENTATION OR WARRANTY EXPRESS OR IMPLIED.

PREPARED BY ALCAN TOXICOLOGY SERVICE
P.O. BOX 1500 JONQUIERE (QUEBEC), CANADA, G7S 4L2 - 418-699-3907
FAX NO: 418-699-2993

N/A : NOT APPLICABLE N/D : NOT DETERMINED DC : DECOMPOSES

14.4 Division 4.3 - Substances which, in contact with water, emit flammable gases

14.4.1 Certain substances on contact with water may emit flammable gases that c... form explosive mixtures with air. Such mixtures are easily ignited by a... ordinary sources of ignition, for example naked lights, sparking handtools or unprotected light bulbs. The resulting blast wave and flames may endanger peopl... and the environment. The following test method is used to determine whether t... reaction of a substance with water leads to the development of a dangerous amou... of gases which may be flammable. The test method can be applied to solid a... liquid substances. It is not applicable to pyrophoric substances.

14.4.2 Test method

14.4.2.1 Principle of the method

The substances should be tested in its commercial form at ambi... temperature (20°C) by bringing it into contact with water. If spontaneo... ignition of the gas occurs at any step, no further testing is necessary.

14.4.2.2 Procedure

14.4.2.2.1 A small quantity (approximately 2 mm diameter) of the test substan... is placed in a trough of distilled water at 20°C. It is noted (i) whether an... gas is evolved and (ii) if spontaneous ignition of the gas occurs.

14.4.2.2.2 A small quantity of the test substance (approximately 2 mm diameter... is placed on the centre of a filter paper which is floated flat on the surface ... distilled water at 20°C in a suitable vessel, i.e. a 100 mm diameter evaporati... dish. The filter paper is to keep the substance in one place, under wh... condition the likelihood of spontaneous ignition of any gas is greatest. It ... noted (i) whether any gas is evolved and (ii) if spontaneous ignition of the g... occurs.

14.4.2.2.3 The test substance is made into a pile approximately 2 cm high a... 3 cm diameter with an indentation in the top. A few drops of water are added ... the hollow. It is noted whether (i) any gas is evolved and (ii) if spontaneo... ignition occurs.

14.4.2.2.4 In the case of a solid substance, the package should be inspected f... any particles of < 500 μm diameter. If that powder constitutes more than ... (mass) of the total, or if the substance is friable, then the whole of the sampl... should be ground to a powder before testing to allow for a reduction in partic... size during handling and transport, otherwise as for liquids the substance shou... be tested in its commercial state. The test should be performed at ambie... temperature (20°C) and atmospheric pressure, and repeated three times.

14.4.2.2.5 Water is put into the dropping funnel and enough of the substance (up to a maximum weight of 25 g) to produce between 100 cm^3 and 250 cm^3 of gas is weighed and placed in a conical flask. The tap of the dropping funnel is opened to let the water into the conical flask and a stop watch is started. The volume of gas evolved is measured by any suitable means. The time taken for all the gas to be evolved is noted and where possible, intermediate readings are taken. The rate of evolution of gas is calculated over 7 hours at 1 hour intervals. If the rate of evolution is erratic or is increasing after 7 hours, the measuring time should be extended to a maximum time of 5 days. The five day test may be stopped if the rate of evolution becomes steady or continually decreases and sufficient data has been established to assign a packing group to the substance or to determine that the substance should not be classified in Division 4.3. If the chemical identity of the gas is unknown the gas should be tested for flammability.

14.4.2.3 Criteria for classification

A substance should be classified in Division 4.3 if:

(a) spontaneous ignition takes place in any step of the test procedure, or

(b) there is an evolution of a flammable gas at a rate greater than 1 litre per kilogram of the substance per hour.

14.4.2.4 Assignment of Packing Groups

(a) Packing Group I is assigned to any substance which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.

(b) Packing Group II is assigned to any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Packing Group I.

(c) Packing Group III is assigned to any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Packing Groups I or II.